



Heteropolyacid encapsulated in $\text{Cu}_3(\text{BTC})_2$ nanocrystals: An effective esterification catalyst

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ABSTRACT

An original synthesis approach to prepare $\text{Cu}_3(\text{BTC})_2$ (BTC = benzene tricarboxylic acid) encapsulated Keggin phosphotungstic acid (HPW) [$\text{HPW}/\text{Cu}_3(\text{BTC})_2$] involving mixing of reagents at room temperature, quenching in liquid nitrogen and freeze drying has resulted in the formation of nanocrystals. The catalytic properties of the as-synthesized nanocrystalline materials were assessed using a model esterification reaction of acetic acid with 1-propanol. $\text{HPW}/\text{Cu}_3(\text{BTC})_2$ catalyst is partially dissolved in presence of acetic acid. In the esterification reaction the molar ratio of acetic acid to 1-propanol is critical. At high molar ratio of acetic acid to 1-propanol (1:2) leaching of Cu^{2+} and HPW was observed. However, at low molar ratio of acetic acid to 1-propanol (1:40) leaching of Cu^{2+} and HPW could be prevented and the catalyst was stable. Nanosized $\text{HPW}/\text{Cu}_3(\text{BTC})_2$ showed higher catalytic activity compared to micron-size $\text{Cu}_3(\text{BTC})_2$ (HKUST-1), ultrastable Y zeolite and micron-sized $\text{HPW}/\text{Cu}_3(\text{BTC})_2$ catalysts. The stability of the nanosized MOF catalyst in acidic reaction medium after esterification reaction was investigated by powder X-ray diffraction (PXRD), scanning electron microscope (SEM) and N_2 adsorption.

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1. Introduction

Metal–organic frameworks (MOFs) are porous crystalline hybrid organic–inorganic materials constructed by metal ions coordinated to multidentate organic ligands leading to three-dimensional extended networks having channels and cavities [1]. Owing to their unique and outstanding properties such as permanent porosity, high surface area and crystallinity, the use of MOFs in various applications, e.g. gas storage [2], separation [3], and catalysis [4] is being explored. The important features of MOF as potential catalyst are its tunable pore size, shape and dimension constructed by the selection of metal and organic linker as the main part of the building blocks. Nevertheless, their use in catalysis has been very much limited owing to limited thermal and moisture stability apart from often completely blocked metal sites by the organic linker or solvent, leaving no free positions available for substrate chemisorption.

In the field of catalytic applications of MOFs, the catalytic activity of $\text{Cu}_3(\text{BTC})_2$ in various organic reactions such as oxidation of *p*-benzoquinone [5], Friedländer condensation between 2-aminobenzophenones and acetylacetone [6], cyanosilylation of aldehydes [7] among others has been reported. Modification of MOF with active metal nodes [8], homochiral MOFs [9], MOF encapsu-

lated metal nanoparticles [10], porphyrin [11] and heteropolyacid (HPA) [12–14] has been carried out extensively for specific catalytic applications exploiting the unique features of MOF. Successful incorporation of Keggin type HPAs in $\text{Cu}_3(\text{BTC})_2$ (HKUST-1) [12,13] and MIL-101 [14] has been demonstrated via impregnation or one-step synthesis. HPA is a molecular template for $\text{Cu}_3(\text{BTC})_2$ (HKUST-1) and room temperature synthesis of $\text{HPW}/\text{Cu}_3(\text{BTC})_2$ has been achieved [15]. Supporting HPA in the host lattice structure of a MOF offers many advantages like isolation of individual Keggin units improving molecular accessibility compared to bulk HPA which has relatively low surface area ($<10 \text{ m}^2 \text{ g}^{-1}$). The heterogenization of the HPA in a MOF crystal enables catalyst recovery and recycling. The use of MOF encapsulated HPA has been reported in oxidation catalysis [16] and hydrolysis [17]. $\text{HPW}/\text{MIL}-101$ has been evaluated for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate and has showed >99% conversion with 100% selectivity after 2 h at 40 °C using toluene as a solvent [18]. Su and co-workers reported high catalytic activity of HPAs/ $\text{Cu}_2(\text{BTC})_3$ in hydrolysis of esters in excess water and showed that the catalyst could be re-used repeatedly without loss of activity [17]. Maksimchuk et al. [16] have demonstrated the use of MIL-101 encapsulated titanium- and cobalt-monosubstituted Keggin HPAs for oxidation of alkenes and showed fairly good catalytic activity and selectivity.

The conventional hydrothermal approach of MOF catalyst synthesis is rather time and energy consuming and often leads to large crystal sizes ($>20 \mu\text{m}$), which are expected to be less suitable for liquid phase catalysis because of intracrystalline mass

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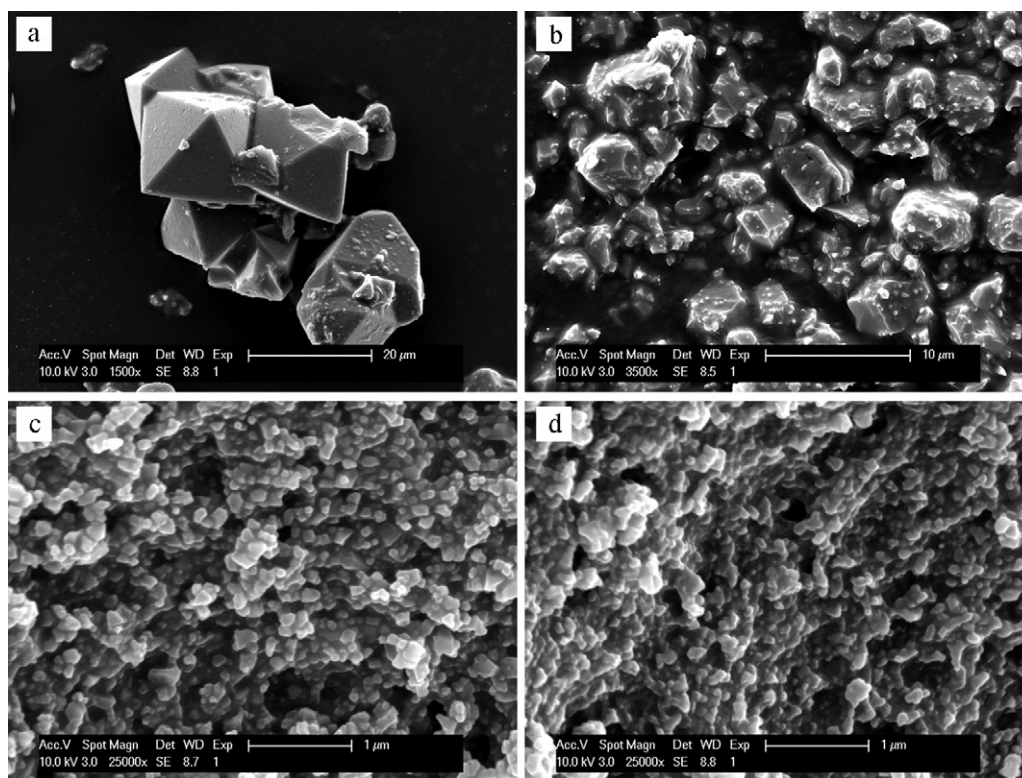


Fig. 1. SEM images of HPW/Cu₂(BTC)₃ materials synthesized (a) hydrothermally, (b) at room temperature for 24 h, (c) at room temperature with quenching in liquid nitrogen of concentrated solution 1 min after mixing of reactants and (d) at room temperature with quenching of diluted solution 1 min after mixing of reactants.

transport limitation. Recently, we reported the preparation of nanosized HPW/Cu₃(BTC)₂ via rapid room temperature synthesis in combination with freeze drying [19]. The as-synthesized HPW/Cu₃(BTC)₂ nanomaterials showed high catalytic activity in the esterification reaction of acetic acid with 1-propanol under mild reaction conditions. The nanomaterials outperformed micron-sized HPW/Cu₃(BTC)₂ and ultrastable Y zeolite (CBV 720). An observed drawback was that acetic acid used in the reaction mixture compromised the stability and solubility of the nano MOF material. Here, we represent a more detailed study on the stability and solubility of the nanosized HPW/Cu₃(BTC)₂ in regards to the concentration of acetic acid used for esterification reaction.

2. Experimental

2.1. Materials

Cu(II) nitrate trihydrate [Cu(NO₃)₂·3H₂O] (puriss. p.a., 99–104%, Sigma–Aldrich), phosphotungstic acid hydrate [H₃PW₁₂O₄₀·nH₂O] (Fluka), 1,3,5-benzene tricarboxylic acid (H₃-BTC) (98%, ACROS), absolute ethanol (BDH), acetic acid (99–100%, Chem-Lab), DMF (99.5%, ACROS) and 1-propanol (99+%, ACROS) were used as received. Ultrastable Y zeolite (CBV-720) was supplied by Zeolyst International and used without further treatment.

2.2. Sample preparation

A solution was prepared by dissolving Cu(NO₃)₂·3H₂O (5.17 mmol, 1.215 g) and H₃PW₁₂O₄₀·nH₂O (0.28 mmol, 0.8 g) in 10 ml of distilled water and H₃-BTC (2.77 mmol, 0.5825 g) in 13.3 ml of absolute ethanol via vigorous magnetic stirring. A more diluted solution was prepared by combining Cu(NO₃)₂·3H₂O (1.44 mmol, 0.349 g) and H₃PW₁₂O₄₀·nH₂O (0.0082 mmol, 0.231 g) in 10 ml of deionised water with H₃-BTC (0.856 mmol, 0.180 g) dis-

solved in 10 ml of absolute ethanol. The solutions were stirred for 1 min and frozen in liquid nitrogen. Lyophilization was performed at 100 Pa for 18 h. The collected solids were washed with water and ethanol mixture [water:ethanol = 1:1 (v/v)] through a series of centrifugation and redispersion steps. The products were dried in an oven at 60 °C for 48 h. For comparison, HPW/Cu₃(BTC)₂ crystals were also synthesized under hydrothermal conditions at 110 °C for 16 h in Teflon-lined stainless steel autoclaves and at room temperature with magnetic stirring for 24 h. Cu₃(BTC)₂ (HKUST-1) samples without HPW were synthesized by mixing 5.17 mmol of Cu(NO₃)₂·3H₂O and 2.77 mmol of H₃-BTC in 23.3 ml of DMF and stirred at room temperature for 24 h.

2.3. Catalyst characterization

The particle size and morphology of the as-synthesized nanomaterials were investigated by SEM on a Philips XL-30 FEG instrument equipped with a tungsten filament. Samples were spread on carbon disc mounted to SEM aluminum pin stubs. Gold was sputtered on the samples prior to analysis. The PXRD patterns were collected using a STOE StadiP diffractometer with Cu Kα1 beam in high-throughput transmission mode. N₂ adsorption isotherms at –196 °C were collected from a N₂ adsorption instrument (Micromeritics Tristar 3000). Before measurements, samples were degassed at 110 °C under N₂ gas overnight.

2.4. Catalytic reactions

Esterification reactions were performed at different molar ratios of acetic acid to 1-propanol corresponding to 1:2, 1:5, 1:10, 1:20 and 1:40. Reactions were performed in closed vials inserted into a copper block. The reaction temperature was set at 60 °C and the content magnetically stirred at 800 rpm. The weight of solid catalysts was 2.3 wt% based on 1-propanol. Aliquots of the reaction

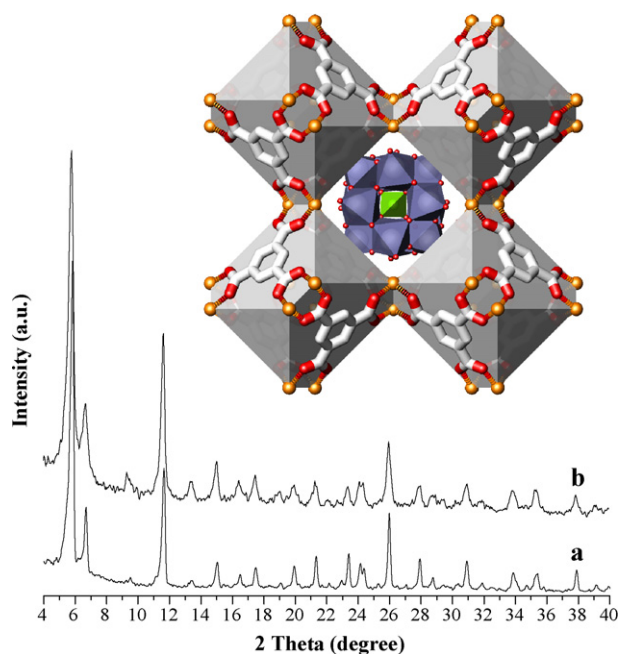


Fig. 2. XRD patterns of HPW/Cu₃(BTC)₂ materials synthesized (a) hydrothermally and (b) at room temperature with quenching in liquid nitrogen of concentrated solution 1 min after mixing reactants. The insert is an illustration of Keggin ion (W-octahedra blue, P-tetrahedron green) in HKUST-1 framework (carbon: white, oxygen: red, copper: orange) as determined from Rietveld refinement [15]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

mixture were withdrawn with a micro-syringe after 7 h. Catalyst was separated via centrifugation prior to gas chromatography analysis performed using a 30 m long Chrompack 8760 WCOT fused silica capillary column and FID detection. After reaction, the catalysts were recovered and washed through a series of centrifugation and re-dispersion steps, and dried in an oven at 60 °C for recycling experiments.

3. Results and discussion

3.1. HPW/Cu₃(BTC)₂ nanomaterial characterization

Fig. 1 shows SEM images of HPW/Cu₃(BTC)₂ materials synthesized from three different synthesis approaches namely hydrothermal synthesis at 110 °C, 24 h room temperature synthesis and 1 min room temperature synthesis followed by freeze drying. According to SEM images (Fig. 1c and d), materials prepared by the freeze drying method were nanosized having an average particle size of ca. 65 and 50 nm for concentrated and diluted synthesis solutions, respectively. These samples were reproductions of previous work [19]. In contrast, the conventional hydrothermal synthesis produced micron-sized crystals with typical octahedral morphology (Fig. 1a). HPW/Cu₃(BTC)₂ crystals synthesized using the long procedure at room temperature had irregular shapes and particle sizes of 1–5 micron (Fig. 1b). To date, only a few MOF nanomaterials have been reported in the literature. For example, Fischer and co-workers [20] reported the preparation of phase pure Cu₃(BTC)₂ having a particle size of about 200 nm obtained from a supersaturated mother solution heated up to 85 °C for 40 min followed by immediate cooling at 25 °C. MOF-5 nanocrystals having a particle size of about 150 nm were successfully prepared via capping with additional surfactant *p*-perfluoromethylbenzenecarboxylate (pfmbc) at room temperature [21]. The authors claimed the pfmbc to compete with the initial 1,4-benzene dicarboxylic acid (BDC) ligand for coordination to the [Zn₄O]⁶⁺ units. Jhung et al. [22] reported

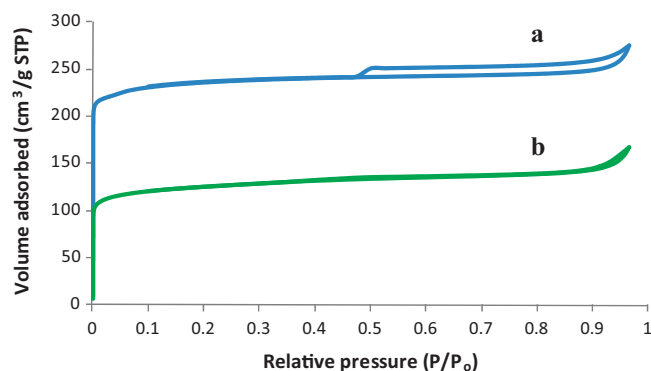


Fig. 3. Nitrogen adsorption isotherms of (a) Cu₃(BTC)₂ (HKUST-1) and (b) HPW/Cu₃(BTC)₂.

microwave synthesis of nanosized chromium terephthalate MIL-101 with an average particle size of about 40 nm. The present method involving mixing at room temperature and freeze drying for the synthesis of nanosized MOF materials is much more convenient compared to the previously reported methods since neither heating nor chemical additives are required. The reported method is very simple and highly reproducible [19].

According to XRD (Fig. 2a), all synthesis methods applied in this study yielded crystalline HPW/Cu₃(BTC)₂ materials, isostructural to HKUST-1 framework [23], accommodating HPW ions in the cavities (Fig. 2, insert). Additionally, broadening of the Bragg reflections was noted for the XRD patterns obtained from HPW/Cu₃(BTC)₂ nanomaterials, further confirming the nano size. The ratio of Cu/P/HPW determined by ICP analysis was 48:5.9:48.6, which is in good agreement with the theoretical ratio of 48:4:48 [15]. Based on nitrogen adsorption isotherms (Fig. 3), the pore volume of the HPW/Cu₃(BTC)₂ is about half of the volume observed for Cu₃(BTC)₂ without HPW (0.36 cm³/g), which is consistent with the reported 100% occupation of one of the two types of large cavities in HKUST-1 structure. Further characterization of the present nanomaterials has been provided in ref. [19].

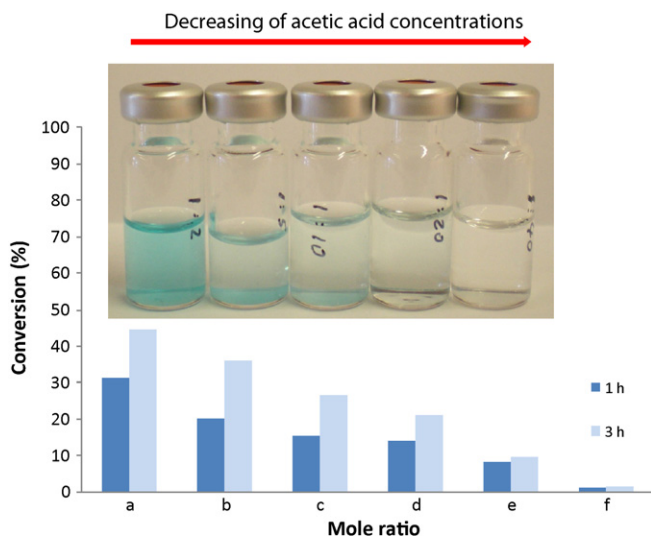


Fig. 4. Conversion of acetic acid catalyzed by 65 nm-sized HPW/Cu₃(BTC)₂ at different molar ratios of acetic acid to 1-propanol (a) 1:2, (b) 1:5, (c) 1:10, (d) 1:20, (e) 1:40 and (f) control experiment with a mole ratio of 1:40. Esterification reaction was performed for 1 h and stopped. The solid catalyst was removed by centrifugation and continued for another 3 h. The insert shows the corresponding digital photos of supernatants obtained after catalytic testing for 1 h performed in different molar ratios of acetic acid to 1-propanol. Reaction conditions: T = 60 °C and 2.3 wt% of catalyst based on 1-propanol with stirring speed set at 800 rpm.

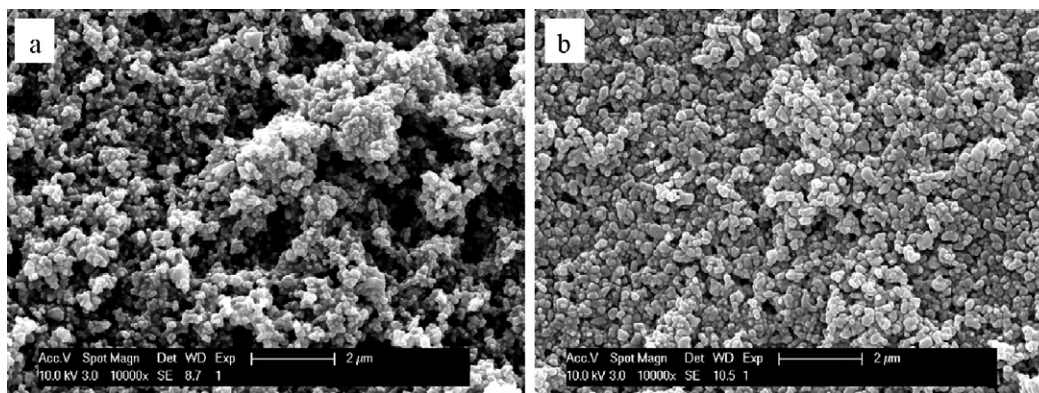


Fig. 5. SEM images of 65 nm-sized HPW/Cu₃(BTC)₂ (a) as-synthesized and (b) after catalytic reaction performed at molar ratio of acetic acid to 1-propanol of 1:2.

3.2. Catalytic performance of HPW/Cu₃(BTC)₂ nanomaterials

The catalytic performance of HPW/Cu₃(BTC)₂ nanomaterials was evaluated in esterification of acetic acid with 1-propanol in the absence of solvent at a reaction temperature of 60 °C. Acetic acid is very aggressive to MOFs as previously reported by Wang and Cohen [24] who demonstrated digestion of IRMOF-3 using acetic anhydride in chloroform. For investigating the stability of HPW/Cu₃(BTC)₂ in the presence of acetic acid under reaction conditions, the esterification reaction was performed using molar ratio of acetic acid to 1-propanol of 1:2, 1:5, 1:10, 1:20 to 1:40. The stability of the nano MOF (65 nm-sized HPW/Cu₃(BTC)₂) and the Cu²⁺ and HPW leaching were investigated by removing the catalyst via centrifugation after 1 h reaction, and verifying the presence of homogeneous phase catalytic activity in the period up to 3 h at reaction temperature. At high concentration of acetic acid with respect to 1-propanol (1:2), leaching of the Cu²⁺ from the HPW/Cu₃(BTC)₂

nanomaterials was noted even visually. The reaction solution after removal of the solids by centrifugation remained blue (Fig. 4, insert). In addition, the occluded HPW were found leached into the solution as further conversion of acetic acid and 1-propanol was obtained after the removal of the solid catalyst (Fig. 4). Although the XRD pattern of the separated catalyst did not reveal significant structure deterioration, significant change in the crystal morphology of the nanosized HPW/Cu₃(BTC)₂ was noted by SEM (Fig. 5b). The particle size of the HPW/Cu₃(BTC)₂ nanomaterials increased from 65 to 100 nm after the first catalytic testing. Surprisingly, the nanocrystals were found to be stable after a second catalytic testing. For comparison, the Cu₃(BTC)₂ (HKUST-1) material in the absence of HPW was used as a catalyst for esterification reaction at a mole ratio of acetic acid to 1-propanol (1:2) under similar reaction conditions. Complete dissolution of the solid catalyst was noted at the end of the test. Furthermore, the Cu₃(BTC)₂ (HKUST-1) was inactive. There was no formation of ester. This observation revealed that the

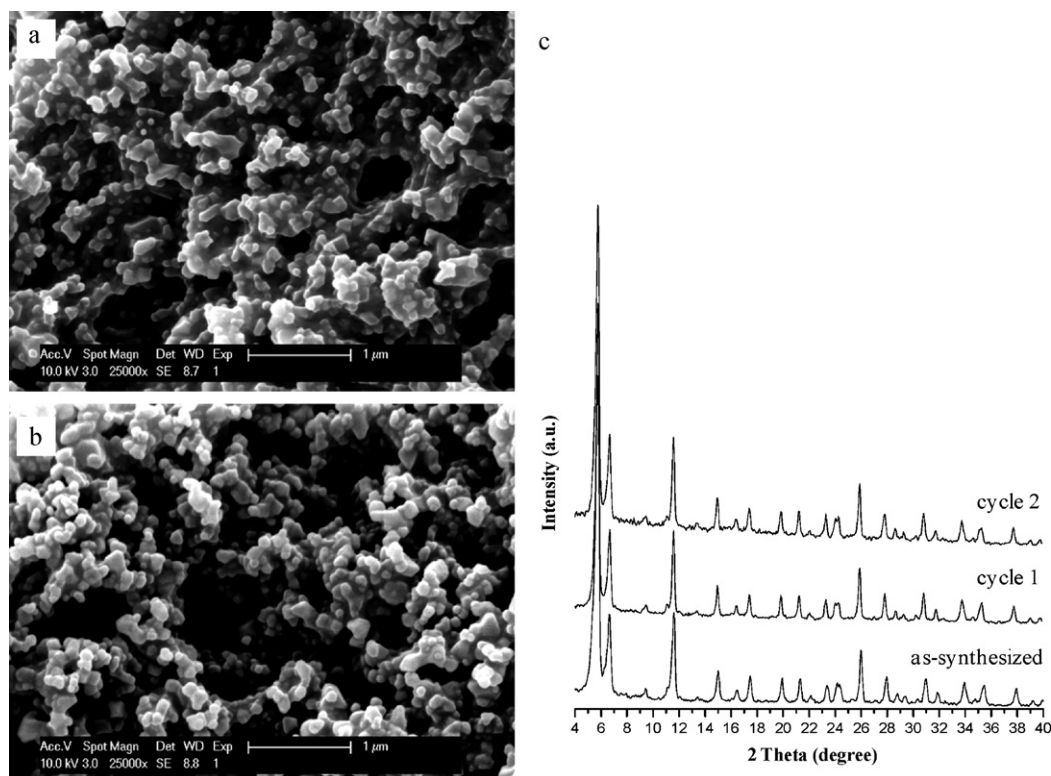


Fig. 6. SEM images of 65 nm-sized HPW/Cu₃(BTC)₂ (a) as-synthesized, (b) after catalytic reaction performed at molar ratio of acetic acid to 1-propanol of 1:40, and (c) the corresponding XRD patterns.

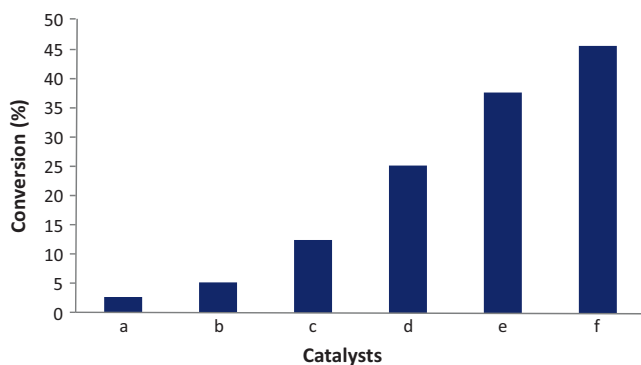


Fig. 7. Esterification reaction of acetic acid with 1-propanol catalyzed by different catalysts: (a) without catalyst, (b) Cu₃(BTC)₂ (HKUST-1), (c) hydrothermally synthesized HPW/Cu₃(BTC)₂, (d) ultrastable Y zeolite (CBV-720), (e) 65 nm-sized HPW/Cu₃(BTC)₂ and (f) 50 nm-sized HPW/Cu₃(BTC)₂ catalysts. Reaction conditions: $T = 60^\circ\text{C}$, mole ratio of acetic acid to 1-propanol at 1:40 and 2.3 wt% of catalyst based on 1-propanol, 7 h reaction time.

Keggin HPW is necessary for catalytic activity, and the copper nodes of the Cu₃(BTC)₂ (HKUST-1) at most play a role for propanol activation. The more limited dissolution of HPW/Cu₃(BTC)₂ showed that the immobilization of the Keggin anions within the HKUST-1 matrix enhanced the framework stability even at high acetic acid concentration. This is in agreement with facile formation of the structure at room temperature and the remarkable synergy between Keggin and the pore structure of this MOF [15].

By increasing the mole ratio of acetic acid to 1-propanol from 1:2 to 1:20, the leaching of Cu²⁺ into the reaction mixture was reduced. Visually a trend of decreasing copper leaching into solution was observed depending on the concentration of acetic acid from blue to pale blue as shown in Fig. 4 (insert). The degree of HPW leaching probed by residual catalytic activity in homogeneous phase after solid catalyst removal following the same trend (Fig. 4). At a mole ratio of acetic acid to 1-propanol of 1:40, colorless supernatant was obtained after centrifugation indicating no leaching of Cu²⁺. Also, no further conversion was noted after removal of the solid catalyst (Fig. 4). Under such conditions the esterification reaction catalyzed over the nanocatalyst is truly heterogeneous without leaching of copper or HPW. The structure, crystal size and morphology of the HPW/Cu₃(BTC)₂ nanomaterials were preserved after catalytic testing under conditions preventing leaching as evidenced by XRD (Fig. 6c) and SEM (Fig. 6b), respectively.

Having identified reaction conditions under which HPW/Cu₃(BTC)₂ is a truly heterogeneous catalyst, the catalytic performance of the nanosized HPW/Cu₃(BTC)₂ was compared with reference catalysts including both micron-sized HPW/Cu₃(BTC)₂ and ultrastable Y zeolite. The mole ratio of acetic acid to 1-propanol was set at 1:40. The catalytic activity at 60 °C was estimated from the conversion of acetic acid after 7 h. The only detected product of the reaction was propyl acetate with a selectivity of 100%. The conversion of acetic acid catalyzed by different catalysts is shown in Fig. 7. The 50 nm and 65 nm-sized HPW/Cu₃(BTC)₂ samples showed higher catalytic activity with 45.4 and 37.7% conversion, respectively, as compared to the reference catalysts ultrastable Y zeolite (25%) and micron-sized HPW/Cu₃(BTC)₂ (12.5%). A control experiment without the introduction of catalyst showed only ca. 3% conversion. Cu₃(BTC)₂ (HKUST-1) catalyst under similar reaction conditions showed negligible catalytic activity. Thus, the results clearly indicated that Keggin HPW species occluded in Cu₃(BTC)₂ pores are significantly active in esterification catalysis. Although the origin of the observed difference in catalytic activity between nano and micron-sized HPW/Cu₃(BTC)₂ catalysts remains elusive, one possible explanation is that the nanomaterials possess

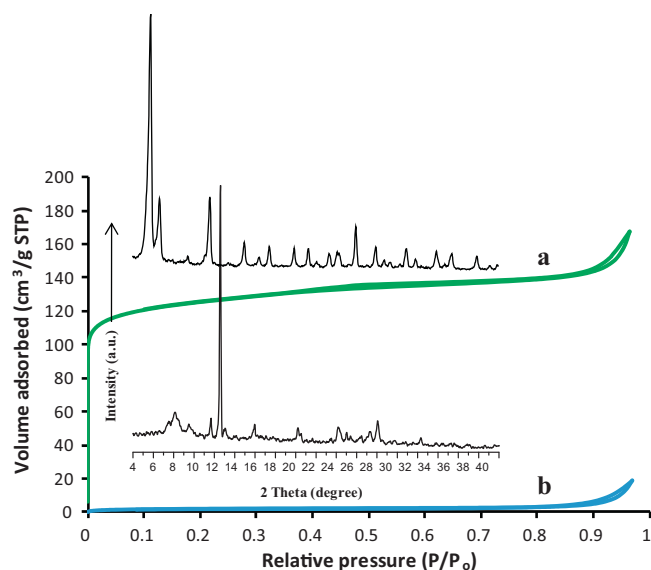


Fig. 8. N₂ adsorption isotherms of as-synthesized 65 nm-sized HPW/Cu₃(BTC)₂ samples washed with (a) water and ethanol mixture [1:1 (v/v)] and (b) water only. The insert shows the corresponding XRD patterns.

a rather shorter intracrystalline diffusional path length, leading to an improved catalytic efficiency.

The porosity of 65 nm-sized HPW/Cu₃(BTC)₂ nanomaterial after two catalytic reactions and recycling was investigated using N₂ adsorption. There was a decline in BET surface area from 392 to 305 m² g⁻¹ after 2 cycles of esterification reaction. This was interpreted as partial pore blocking by products and side products, as well as some limited sintering. This moderate loss of surface area might be responsible for the minor loss of catalytic activity in consecutive runs. A similar observation of a gradual loss of surface area has been reported for HPW/MIL-101 catalyst after use in cyclohexene oxidation performed at 50 °C [16]. It shall be mentioned that the nano catalyst is stable in common organic solvents such as ethanol, DMF, acetonitrile, dioxane and toluene at 65 °C with stirring up to 10 h. Continuous washing with water at room temperature causes structure deterioration as evidenced with XRD and N₂ adsorption (Fig. 8).

4. Conclusions

A facile though highly reproducible method was demonstrated for the synthesis of nanocrystalline HPW/Cu₃(BTC)₂. The crystallization at room temperature is extremely fast and is achieved within minutes. The crystal growth can be interrupted via freezing of the suspension in liquid nitrogen. Lyophilization is convenient for recovering of the MOF product. The HPW/Cu₃(BTC)₂ nanomaterials with particle size of ca. 50 nm is an exceptional catalyst that outperforms a reference zeolite in the model esterification reaction of acetic acid with 1-propanol at 60 °C. Provided a high ratio of 1-propanol to acetic acid of 40:1 is used, HPW/Cu₃(BTC)₂ behaves as a true heterogeneous catalyst. Some decrease of BET surface area was noted after catalyst reuses even under optimized reaction conditions and resulted in a gradual loss of catalytic activity after been reused for several cycles, although the crystallinity and structure were well preserved. The catalyst is unstable, however, at high concentrations of acetic acid.

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